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14. ABSTRACT In the period of this project there have been significant advances in the development and application of second harmonic and sum frequency generation to the investigation of equilibrium and time dependent processes at aqueous interfaces. A powerful way to determine the dynamics of molecular motion of both interfacial solvent and adsorbed solute molecules, which is of major importance in interfacial chemistry, e.g. electron transfer, has been achieved using both SFG and SHG. The first demonstration experiments in which molecules are pumped into					
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Report Title

Nonlinear spectroscopy of nanoparticle/aqueous interface

ABSTRACT

In the period of this project there have been significant advances in the development and application of second harmonic and sum frequency generation to the investigation of equilibrium and time dependent processes at aqueous interfaces. A powerful way to determine the dynamics of molecular motion of both interfacial solvent and adsorbed solute molecules, which is of major importance in interfacial chemistry, e.g. electron transfer, has been achieved using both SFG and SHG. The first demonstration experiments in which molecules are pumped into excited electronic states and probed with femtosecond SFG has been accomplished. With these methods the rise and decay of short lived chemical species were detected. The effects of charged surfactants, high concentrations of salts, and heavy water (D₂O) vs (H₂O) interfaces, on adsorbate orientational and solvation dynamics in water have been measured. In addition the dynamics of electron transfer at an organic liquid/water interface have been performed. SHG/SFG experiments at air/water interfaces have measured: polarity at a polystyrene sulfonate/water interface, acid-base equilibria at polystyrene nanoparticle carboxylate/water interface, the presence of organic ions at the air/water interface, and the structure of water beneath an acetonitrile monolayer at the air/acetonitrile solution interface has been investigated.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Solvation dynamics at air/water interface with time resolved sum frequency generation, J. Phys. Chem. C, 2010 DOI:10.1021/JP105223J

Ultrafast intermolecular energy in heavy water. PhysChem-ChemPhys. 2009, 11(40), 9033

Organic ions at the air/water interface. Chem. Phys. Lett. 2009, 477(4-6), 241

Water structure at air/acetonitrile aqueous solution interfaces, J. Phys. Chem. 2009, 113(32)

In plane molecular rotational dynamics at a negatively charged surfactant/aqueous interface. J. Phys. Chem. C. 2008, 112(51), 20375

Second harmonic studies of ions crossing liposome membranes in real time. J. Phys. Chem. B 2008, 112(48), 15263

Oriental motions of vibrational chromophores in molecules at the air/water interface with time resolved sum frequency generation. J. Phys. Chem. B 2008, 112(430), 13572

Protonation at the aqueous interface of polymer nanoparticles with second harmonic generation. J. Phys. Chem. C 2008, 112(40), 15809

Number of Papers published in peer-reviewed journals: 8.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Spectroscopic evidence of organic ions at the air-water interface. 2009, Abstracts, 238th ACS National Meeting, Washington, D.C.

Polarity of polystyrene colloid/aqueous interface with second harmonic generation spectroscopy. 2009, Abstracts, 238th ACS National Meeting, Washington, D.C.

Liposome/aqueous interface. 2009, Abstracts, 237th ACS National Meeting, Salt Lake City, UT.

Orientational motions of chemical groups at the air/water interface. 2009, Abstracts, 237th ACS National Meeting, Salt Lake City, UT.

Water interfaces. 2008, Abstracts, 236th ACS National Meeting, Philadelphia, PA.

From Liposomes to Live Nerve cells. 2008, Abstracts, 40th Middle Atlantic Regional Meeting of the American Chemical Society, Queens, NY

Molecules at aqueous interfaces. 2008, Abstracts, 235th ACS National Meeting, Washington, D.C.

Equilibrium and ultrafast phenomena at liquid interfaces. 2007, Abstracts, 234th ACS National Meeting, Boston, MA.

Nanoparticle to microparticle to live nerve cell tissue aqueous interfaces. 2007, Abstracts, 233rd ACS National Meeting, Chicago, IL.

Determination of rotational dynamics at the air/D2O interface by time resolved second harmonic generation. 2007, Abstracts, 233rd ACS National Meeting, Chicago, IL.

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Graduate Students

NAME	PERCENT SUPPORTED
Eric McArthur	0.33
Mahamud Subir	0.33
Kim Nguyen	0.33
Sung Young Hong	0.33
FTE Equivalent:	1.32
Total Number:	4

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Yi Rao	0.33
Man Xu	0.33
Louis Haber	0.33
Saonli Basu	0.33
FTE Equivalent:	1.32
Total Number:	4

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Nicholas J. Turro	0.00	Yes
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>	
Jian Liu	
Mahamud Subir	
Eric McArthur	
Kim Nguyen	
Total Number:	4

Names of other research staff

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

We have made significant progress in advancing the development of a molecular level description of the chemical and physical properties of liquid interfaces, with an emphasis on aqueous interfaces, air/water, organic liquid/water, and liquid/solid interfaces. The interfaces that we have studied include both planar interfaces and the interfaces of nanoparticles suspended in water. The primary methods that we have employed are the interface selective second harmonic generation, SHG, and vibrational sum frequency generation, SFG, spectroscopies, to investigate equilibrium and ultrafast phenomena at interfaces. These two spectroscopies complement each other in that SFG is a nonlinear vibrational spectroscopy and thus has the proven analytical chemistry properties of Raman and IR spectroscopies to identify species, their populations, their structure and local intermolecular interactions. The complementary value of SHG is that it is an electronic state spectroscopy that can elicit the electronic structure of molecules and thereby properties that are sensitive to their electronic states, i.e. their ground and excited electronic states

NANOPARTICLES IN AQUEOUS SOLUTION

For bulk media the area of the interface that separates the two media is very small relative to the volume of bulk phases. In contrast, nanoparticles have a much higher surface area to bulk volume ratio which confers special properties, e.g. electronic structure (surface plasmon resonances), catalytic activity of metal nanoparticles, and the much larger adsorbate population on adding together the areas of each particle, than is found at the planar interface^{1,2}. Another characteristic of nanoparticles is that they can organize themselves in interesting ways if they consist of various molecular species³⁻⁵. As examples are oil in water emulsions, liposomes and polymer beads³⁻⁶. We have used SHG and SFG to investigate significant features of various nanoparticles. *I.*

Acid-base chemistry at aqueous/polymer nanoparticle interfaces

The acid-base chemistry at the surface of a nanoparticle determines its charge density, which thereby, affects the population of charged and polar species in the interfacial region. Similarly it affects the adsorption and binding of diverse chemical species and alters the structure and orientation of the molecules at the interface. We have employed an SHG method, developed in our laboratory, to measure the electrostatic potential, the pH, and the acid-base equilibrium of the carboxyl (-COOH) functional group fixed at the surface of polystyrene carboxyl, PSC, particles of 457nm radius, suspended in bulk water. This method is based on our discovery that the electric field of a charged interface polarizes the bulk water molecules and generates a significant SHG signal by a third order process, often referred to as the $\chi^{(3)}$ method where $\chi^{(3)}$ is the third order susceptibility. We found that the SHG electric field can be expressed as, $E_{2\omega} = A + B \Phi$ where A is the total second order contribution and B is the effective third order contribution due to the polarized water, and Φ is the electrostatic potential at the charged surface plane. For an acid-base reaction the surface charge is determined by the density of the charged form, which for PSC is the negatively charged base, -COO⁻. The SHG electric field is linearly proportional to the surface electrostatic potential, Φ , which in turn depends on the degree of acid-base ionization. With the $\chi^{(3)}$ method we obtain the absolute value of the electrostatic potential, the interface pH, and the interfacial equilibrium constant, K_a of the surface carboxyl acid. We found that the equilibrium constant is a factor of 4 smaller than that of a long chain carboxylic acids. This decrease in acidity at the interface reflects a decrease in electrostatic repulsions among the charged -COO⁻ groups when their density is diminished. A decrease in the interfacial equilibrium constant achieves this, which means a lower surface free energy.

Organic ions crossing membranes in real time

Liposomes are lipid bilayer particles that are of wide spread interest and significance in diverse areas of science and technology ranging from their use as biological membrane models, to catalysis, solar energy conversion, and drug delivery agents. In all of these fields it is the bilayer membrane property of separating the inner water compartment from the external aqueous solution in such a way that it is selective in allowing passage of certain chemical species from the external solution across the bilayer to the inner compartment and the reverse process. The liposome membrane has this selectivity because the interior is a hydrophobic region. Therefore, for a chemical species to pass from water into the membrane requires some nonpolar feature. We therefore see that for species such as alkali ions the energy barrier to go from its solvated form in water into the hydrophobic region is too high except at very high temperatures, in which case the liposome will break apart. It is of significance that although small ions cannot cross the membrane there are organic ions, e.g. many peptides in biology that can traverse the membrane⁴. The transmembrane movement of ions is central to the properties of the particular liposome being investigated. In our studies we have demonstrated that the movement of chemical species can be monitored using the SHG method in real time. The molecule that we have chosen to study is the triphenyl cationic dye malachite green, MG^+ , and the liposome is made up of dioleoylphosphatidyl glycerol, DOPG, molecules. The MG^+ was selected because it has a large hyperpolarizability. The DOPG was selected because it is a negatively charged liposome, as are most biological cells, and it is easy to obtain a monodisperse size distribution, which in our experiments had a diameter of 110 ± 5 nm. The basic idea of the method derives from the fact that molecules oriented in one way on the outer leaflet of the bilayer have the opposite orientation on the inner leaflet because of symmetry. The oppositely oriented molecules have the opposite sign in their hyperpolarizabilities; consequently, they will cancel and not produce a SHG signal. We will use this property to measure transmembrane movement in real time. In our experiments an aqueous solution containing the liposomes is rapidly mixed with an aqueous solution containing MG^+ . The adsorption of MG^+ to the outer leaflet of the liposome occurs in less than one second, i.e. the rise time of the SHG signal is faster than one second. As MG^+ crosses to the inner membrane and adsorbs to the inner leaflet the SHG signal is decreased because of the opposite orientations. We found that the SHG signal did not approach zero as would occur if the outer and inner populations approached equality, taking the different surface areas into account. Why was this not taking place? We proposed a model based on our establishing that MG^+ crosses the membrane without its counter ion. Because of this the MG^+ in the inner compartment produces a positive potential that increases as more MG^+ cross which thereby opposes MG^+ , which is a cationic dye, from crossing to the inner compartment. We thus have a concentration gradient that drives MG^+ in and a growing positive potential that drives it out. The balance of these opposing factors is thus responsible for the SHG signal not decaying to zero. To test this model we introduced ionophores into the system. Ionophores have the capability to transport ions. The ionophores could eliminate the positive potential by transporting an alkali ion or hydronium ion from inside to outside as MG^+ crossed in. We first used the antibiotic valinomycin (VAL) which transports alkali ions but not hydronium ions. On adding VAL to the solution at a concentration of 10^{-8} M we observed that the SHG signal decayed rapidly towards zero. This supported our model of the balance between the opposing concentration and electrostatic forces. Following this work we decided to investigate the behavior of other ionophores. Testing the antibiotic carbonyl cyanide-m-chlorophenyl hydrazone (CCCP), an ionophore, which only transports protons, we found that it had a very small effect. This result was anticipated because the deprotonated form of CCCP is negatively charged and as a consequence its transport against the negative potential at the outer liposome surface is energetically unfavorable. We then tried the

fascinating antibiotic peptide gramicidin A, gA, which does not carry ions across but rather forms a channel across the membrane allowing alkali and hydronium ions to cross the membrane⁴. The kinetics of SHG decay and its final steady state decay were attributed to the time for insertion of gA into the membrane and having some of the gA flipping from the outer to the inner leaflet, as required to form a channel.

Noble metal nanoparticles

The unique optical and electronic properties of metallic nanoparticles have led to both fundamental science and technology investigations ranging from enhancing optical signals, to theoretical treatments of their optical properties and its dependence on nanoparticle structure, to the development and use as biological and chemical sensors. In our research on gold nanorods (20 x 52nm) at interfaces and in bulk water we have results on their SHG and SFG spectroscopies. At the air/water interface we observed dipolar and quadrupolar surface plasmon resonances in the SHG spectra using the polarization of the SHG to differentiate these resonances. In both the air/water and bulk water experiments more peaks were observed in the SHG spectra than in linear absorption spectra. The assignments of the various peaks are under investigation. An interesting result was observed in SFG studies of the gold nanorods at an air/acetonitrile-water interface. Under the conditions of our experiments the surface was an acetonitrile monolayer. The interfacial intensity from the nitrile stretching vibration, —CN , showed an increase in intensity by a factor of 6 in the presence of the gold nanorods. This intensification is an electromagnetic enhancement due to the coupling of the incident and SFG light with surface plasmons. It should be noted that the correct value for the enhancement of the SFG signal should be much larger than 6 because most of the interfacial acetonitrile molecules are not near the gold nanorods and would therefore not generate an enhanced SFG signal.

WATER STRUCTURE BENEATH AN ACETONITRILE MONOLAYER AT THE AIR/ACETONITRILE-WATER INTERFACE

The interfacial structures, as well as the bulk structure of binary non-electrolyte aqueous solutions are of importance in many areas of chemistry including synthesis chromatography and electrochemistry. Of these, the bulk properties of acetonitrile-water solutions have been extensively studied using many techniques. This has not been the case for the air/acetonitrile water interface. To investigate the air/acetonitrile-water solution interface we used SFG to obtain the vibrational spectra and orientation of the interfacial acetonitrile molecules. These molecules are strongly adsorbed to the air/acetonitrile-water solution interface because of the high surface free energy of interfacial water molecules as seen in the high surface tension of water. An unexpected result was obtained. It was found at bulk acetonitrile mole fractions below 0.07 that the —CN group is hydrogen bonded and that the orientation of its symmetry axis is tilted $40\pm$ from the interface normal. On increasing the acetonitrile mole fraction from 0.07 to 0.1 we observed an abrupt change in orientation from $40\pm$ to a tilt of $70\pm$. Concomitant with the abrupt change in orientation on increasing the acetonitrile mole fraction was the abrupt frequency shift of the $\text{—C}^{\text{a}}\text{N}$ vibration from being hydrogen bonded to not being hydrogen bonded. The abrupt change occurred in the region of full acetonitrile monolayer coverage, which was at a mole fraction of 0.07 to 0.1 where the acetonitrile excess obtained from surface tension and the Gibbs equation, has its maximum value. The model proposed to describe this abrupt change is that as the density of interfacial acetonitrile increases the distance between molecules decrease and the acetonitrile dipole-dipole repulsions become stronger for neighboring dipoles oriented at $40\pm$. This increasing repulsion finally causes an abrupt change in the orientation of the dipoles to a tilt angle of $70\pm$, which is no longer repulsive but in fact is attractive. In our previous studies we examined the structure and spectra of the acetonitrile molecules at the air/acetonitrile-water interface. In

our more recent studies we sought to determine how the water structure changed as the water molecules were displaced from the interface by acetonitrile. Although there are still controversies regarding water structure it is, with some exceptions, accepted that there are three major types of stretches. One corresponds to the “free” OH stretch of water molecules, projecting into the air phase with one of its OH bonds hydrogen bonded. The peak frequency is at 3700 cm^{-1} . The vibration at 3450 cm^{-1} is attributed to weakly hydrogen bonded water molecules and the vibration centered at 3200 cm^{-1} is the more strongly bonded water molecules, which being similar to ice at 3200 cm^{-1} is called the “ice like” structure. As we increased the acetonitrile mole fraction the water SFG spectra changed in intensity. A decrease in the intensity of both the weakly hydrogen bonded water (3450 cm^{-1}) and the more strongly hydrogen bonded water (3200 cm^{-1}) was detected. However, the decrease in the more strongly hydrogen bonded water molecules was more rapid than for the more disordered region (3450 cm^{-1}). At an acetonitrile mole fraction of 0.1 there is no longer a resonant contribution from the hydrogen bonded regions of the SFG spectra. This indicates that the water molecules beneath the acetonitrile monolayer are disordered. Turning to the “free” OH stretch at 3700 cm^{-1} we found that although it decreased as the acetonitrile density increased there remained a resonance that was weaker by a factor of ~ 5 at 3700 cm^{-1} . The observation that there was a resonance at 3700 cm^{-1} indicates that there are oriented water molecules in the interfacial region. Perhaps there are water molecules penetrating the acetonitrile layer and therefore would be “free,” i.e. not hydrogen bonded and have a peak at 3700 cm^{-1} . In any case further work is needed to test these suppositions.

ORGANIC IONS AT THE AIR/WATER INTERFACE

Understanding the propensity of ions for the air/water interface is of great fundamental and practical importance. The earth’s air/water interface is rich in both inorganic and organic ions as are atmospheric aerosols, and of special interest are organic liquid/aqueous interfaces. The reason is that chemical reactions of organic molecules, which are not soluble in water, can react at the organic liquid/water interface with molecules or ions in the aqueous phase. In fact it has been found that many reactions between organic molecules that are not soluble in water are greatly enhanced in the presence of water. For example, it has been found that the Diels-Alder reaction rate constant was 18 times larger when water is present than in the organic solvent toluene. The reason for this enhancement is not known but various models have been proposed. One very useful probe of adsorbates at planar interfaces is provided by surface tension measurements. Despite its value it is limited by the fact that it cannot differentiate the species present at the interface, and thus which ones determine the surface tension. A significant example is the air/electrolyte interface of a bulk solution containing sodium and iodide ions. From surface tension measurements it was inferred that there is a deficiency of ions at the interface. Recent experimental results and molecular simulations have shown and predicted that there is a significant population of iodide ions at the interface. Similar difficulties apply to the presence of organic ions at aqueous interfaces. From surface tension measurements of a solution containing the acid-base pair phenol ($\text{C}_6\text{H}_5\text{OH}$) – phenolate ($\text{C}_6\text{H}_5\text{O}^-$) at a pH in the range of 11 to 12 it was inferred that phenolate ions at the air/water interface are responsible for the decrease in surface tension. It was assumed that it was the phenolate ions because at bulk pH values in the 11-12 range the bulk phenol concentration is 10 to 100 times greater than that of phenolate. The difficulty with the assumption that there is only phenolate at the surface because the phenolate concentration in the bulk is so much larger than phenol is that the pK_a at the surface is the same as in the bulk solution, which it is not. To resolve the issue of what is at the interface we used vibrational SFG spectroscopy to measure the vibrational spectra of interfacial phenol and phenolate which differ in the range of 1230 cm^{-1} to 1300 cm^{-1} . In this SFG experiment a picosecond visible pulse at 800nm is

overlapped in time and space at the interface. The SFG signal generated at the interface is the sum of the visible and IR frequencies. When the IR frequency is equal to the frequency of a vibrational chromophore in an interfacial molecule there is a very large increase in the SFG intensity. By scanning the IR frequency we find peaks in the SFG signal that correspond to the vibrational frequencies of the interfacial molecule. Applying the SFG method we found that the vibration of the carbon-oxygen bond is different for phenol —C—OH and phenolate —C—O— . The peak of the —C—OH vibration is at 1256 cm^{-1} and the peak of the —C—O— vibration is at 1281 cm^{-1} . The phenolate is blue shifted with respect to phenol because of the increase in electron density in the carbon-oxygen bond compared with that in phenol. The SFG spectral results demonstrate that there is a significant population of phenol at the interface up to a bulk pH of 12.9.

Femtosecond UV-Visible Pump/Femtosecond SHG-SFG Probe of Ultrafast Phenomena

To describe interfaces on a molecular level requires in addition to equilibrium properties knowledge of time dependent processes. The most important are molecular motions, energy relaxation, and the dynamics of chemical reactions. To investigate these properties the method generally used is the photo-excitation of interfacial molecules by femtosecond pump pulses followed by probing the photo-excited interface using a time delayed femtosecond probe pulse that generates a second harmonic signal at that delay time. The experiment is repeated at different delay times. The intensity and polarization of the SHG light as a function of time delay is used to record the time evolution of the ensemble of excited and unexcited interfacial molecules. This method is generally referred to as the pump-SHG probe method. It would of course be valuable to use SFG to probe the time evolution of the interface as a complement to the pump-SHG probe method. Nonetheless there have been few pump-SFG probe studies and these pioneering experiments focused on IR pumping of vibrations in the ground electronic state and probing with SFG to follow the vibrational energy relaxation of the interfacial molecules. In the work reported here, we describe the first experiments in which interfacial molecules are pumped to excited electronic states and probed with time resolved SFG. The time resolved SFG experiments involve an 800nm light pulse overlapping in time and space at the interface generating an SFG signal that is the sum of their frequencies. The femtosecond time resolution is achieved by the 800nm and IR pair of pulses reaching the interface at various delay times with respect to when the pump pulse photo-excited interfacial molecules.

Molecular Rotation at Interfaces

The ultrafast process that we studied was the rotational motion of a chemical group, the carbonyl —C=O in the aromatic ring of a coumarin dye molecule, C314, at the air/water interface. We were able to probe the carbonyl group by selecting the frequency of the IR light to be equal to the frequency of the —C=O vibrational stretch frequency of the interfacial molecule, which we obtained from the SFG spectra. The idea of the experiment to measure rotational motions was to use a polarized pump pulse that would preferentially excite molecules of a given orientation within the equilibrium orientational distribution of molecules. This perturbation creates a non-equilibrium orientational distribution. With the SFG probe we monitor the rotational motions towards equilibrium recognizing that the strength and the polarization of the SFG signal is dependent on the orientations of the molecules at the time of the probe measurement. In these orientational relaxation experiments it was the rotation of the —C=O bond axis with respect to the interface normal that was detected. The orientational relaxation time was found to be $220 \pm 20\text{ps}$, which is slightly faster than the orientational relaxation of C314 in the bulk solution. A good example of the value in carrying out both SFG and SHG measurements is seen in the C314 orientational relaxation studies. On performing pump-SHG measurements of the orientational relaxation

time of the C314 we obtained a value of 343 ± 13 ps. The reason for the difference is that in the SHG probe experiment it is the rotational motion of a different axis, namely the permanent dipole moment axis of C314 with respect to the interface normal that is being measured. These results indicate that rotational motions of C314 about different molecular axes experience different friction because there are different barriers for pushing solvent molecules, in one direction vs. another. In other words the rotational motions of the adsorbate reflect an orientationally dependent friction. Perhaps this is not surprising in that the anisotropic forces exerted against a molecule at an interface could favor some motions over others. It is to be noted that by combining the SHG and SFG dynamics we have recently been able to obtain the rotation of third axis (perpendicular to the C314 plane), which means we have succeeded, for the first time, to measure the rotations of the whole molecule in the anisotropic environment of an interface.

Solvation Dynamics

The time dependent rearrangement of solvent molecules in response to the change in the dipole moment of a polar molecule on photoexcitation constitutes solvation dynamics, which is of importance in chemical reactions, especially those that involve charge transfer. Solvation dynamics at the air/water interface reflect the time dependent changes in the asymmetric interfacial network of hydrogen bonding structures. SFG experiments on the solvation dynamics of coumarin 314 at the air/water interface were carried out. The carbonyl stretch was selected in the SFG experiments by tuning the incident IR to be resonant with the carbonyl stretch frequency. The solvation dynamics consisted of two components, one was at 230 ± 40 fs and the other at 2.2 ± 0.3 ps. The interfacial solvation times were slower than the two corresponding components obtained in bulk water, with the slowest interfacial time constant being roughly a factor of two slower than the slowest bulk time constant. An unanticipated result, which we are presently examining, was that the solvation dynamics obtained from SHG measurements was the same as from SFG within our experimental error for both the faster and slower components. However the amplitudes of the two components obtained from SFG and SHG differed significantly. For SFG the amplitude of the faster component is 0.26 and the slower component is 0.74, whereas for SHG the amplitude of the faster component is 0.65 and the slower one is 0.35; the amplitudes obtained by the two methods are reversed. The effects of solvation on the SHG and SFG signals is due to the change in the energies of the electronic states as the solvent rearranges about the excited state molecules. This change in electronic state energies with time changes the SHG hyperpolarizability and the SFG hyperpolarizability. Because there are several susceptibility elements that contribute to the SHG signal, even at resonance with 2ω , it is not clear that it should have the same time dependence as the SFG case where there is only one susceptibility element. In addition to the above results we found that solvation of the excited state molecule did not involve any significant rearrangement of solvent molecules about the carbonyl group, i.e. the energy of the excited state carbonyl stretch vibration did not change. Within our experimental accuracy we observed no new spectral feature on photoexcitation aside from a bleach of the SFG signal at the ground state carbonyl vibrational frequency as expected.

Electron Transfer at an Organic Liquid/Water Interface

The time resolved SFG method has been used to investigate intermolecular electron transfer at a N,N-dimethylaniline,DMA,(liquid)/water interface. Femtosecond photoexcitation of interfacial coumarin, C314 molecules, at the interface initiates an electron transfer reaction in which a ground state DMA donor molecule transfers an electron to an excited singlet state

C314 acceptor molecule. We have selected DMA to serve as the organic liquid in the DMA/water interface to minimize any contribution of reactants translational diffusion to the electron transfer kinetics. The electron transfer time was found to be 16 ± 2 ps. These experiments are the first observations in real time of electron transfer at a liquid/liquid interface.

EXPERIMENTAL *SHG setup* The experimental configuration for SHG measurements consisted of a Nd:YVO₄ solid state laser (Spectral-physics, Millennia Vs) pumped Ti:Sapphire laser (KMLab), which provided 50fs 8 pulses with an energy of 4nJ per pulse at 836 nm with a repetition rate of 82 MHz. The femtosecond laser pulse train was passed through a polarizer, and then focused into the sample in a 2 mm quartz cuvette using a lens with a focal length of 50 mm. A red filter was used between the sample and the lens to block all the stray light at twice the frequency of the laser light. The incident light was S polarized. The generated SHG signal was collected in the forward direction and sent into a monochromator (CVI). Before the monochromator, a blue filter was used to block the residual fundamental laser light. The detection and data acquisition was made possible using a PC connected to a single photon counter and a PMT. *SFG setup* Briefly, an 800nm regeneratively amplified Ti:sapphire system (Spitfire, Spectra Physics) seeded with a MaiTai 80MHz, 80fs oscillator, at a one kilohertz repetition frequency was employed in the present experiments with a typical output power of 2.3mw per pulse. A 70% of output light from the amplifier is introduced into an OPA to generate a signal and idler light. By difference frequency generation in a 1mm AgGaS₂ crystal, tunable infrared light between 3 μ m and 8.5 μ m with a bandwidth of about 150 cm⁻¹ was generated. The IR beam with a typical power of 2uJ per pulse at 8 μ m and is focused onto the sample by a BaF₂ with a 100mm focal length at an angle of $67 \pm$ relative to the surface normal and a spot size of around 150 μ m. The 800nm picosecond light with a typical power of 35uJ per pulse was generated by a home-built pulse shaper and is focused to 210 μ m spot size by a BaF₂ lens with a 250mm focal length at an angle of $76 \pm$ from the surface normal. A 0.3 m spectrograph with a grating of 1200 grooves/mm with 500nm blazed was used. One exit was configured for detecting the dispersed signal with a liquidnitrogen cooled, back-thinned charged coupled device (CCD) camera (Roper Scientific, 1340 \times 400 pixels operating at $-120 \pm$ C. **CONCLUSIONS** Interfaces are of great importance both in fundamental science and technology because of their unique chemical, physical, and biological properties. However because they are molecularly thin structures the application of the traditional and powerful spectroscopic methods, which include electronic absorption, emission, IR, Raman, and magnetic resonance, cannot be used. The bulk overwhelms any interfacial optical signals. It is for this reason that the nonlinear optical spectroscopies, namely Second Harmonic Generation (SHG), and Sum Frequency Generation (SFG), which have the key property of being interface selective, and forbidden in bulk centrosymmetric and isotropic media, have become powerful tools in the investigation of interfacial phenomena. With these spectroscopies we have demonstrated that they can be used to investigate what is arguably the most important class of chemical reactions, proton transfer. We have measured the pK_a of acid-base reactions at the air/water interface and now at the surface of a polymer bead in bulk water. These acid-base reactions are markedly different at aqueous interfaces from that in bulk aqueous solutions. With SHG we have shown how the transport of an organic cation across the phospholipid bilayer of a liposome can be monitored in real time. This method is of potential value in the testing of transmembrane dynamics of chemical species of interest in biology, in drug delivery and in

the sequestering of pollutants. We have addressed the question of what organic ions are present at the air/water interface; a topic of importance at the air/ocean-river-lake water interface, as well as in atmospheric aerosols. SFG has enabled us to resolve a hotly debated issue as to whether or not phenolate and not phenol is at the interface when the bulk pH is 11 to 12. We note parenthetically that phenolate is an important decontaminant of toxic agents. Using SFG to obtain the interfacial spectra of phenol and phenolate enabled us to differentiate them and thus determine their interfacial activity. This settles the controversy as to which form is at the interface at a high pH. We found that the neutral form, C_6H_5OH , is present at the air/water interface even at high bulk pH values. Once again with SFG we were able to measure the vibrational spectrum of other interfacial molecules, which in this case was CH_3CN at the air/water interface. On adding gold nanorods we found a significant enhancement, factor of 6, in the $-C^{\alpha}N$ vibrational SFG intensity. It is well established that acetonitrile molecules displace water molecules at the air/acetonitrile-water interface, thereby lowering the surface free energy. We have used SFG in earlier studies of this widely used solvent mixture to observe the changes in the orientation and vibrational frequency of acetonitrile as its interface population increases. We have now investigated what happens to the water structure beneath the acetonitrile as a full acetonitrile monolayer develops. We found that oriented hydrogen bonding decreased but at the same time obtained some unexpected results. In our efforts to measure ultrafast phenomena we have performed the first experiments in which interfacial molecules are pumped into excited electronic states and their time evolution probed with SFG. This advance provides a new way to investigate ultrafast interfacial processes, which unlike SHG is a vibrational spectroscopy benefiting from the analytical chemistry sensitivity of a vibrational spectroscopy. In using SFG we showed how the rotational motions of an organic adsorbate at the air/water interface can be monitored. With SFG we can turn to different vibrational chromophores and determine their local interactions. Together with SHG as the probe we discovered that rotations about different molecular axes are considerably different. The measured time constants reveal that the friction experienced by the adsorbate depends strongly on the direction of the rotational motion. This could have some bearing on the reaction dynamics between interfacial molecules that are sensitive to their mutual orientation. **ACKNOWLEDGEMENTS** The authors wish to thank DTRA – W911NF-07-1-0116 for their support.

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